cooled to −60°, was added 14.5 ml of *n*-butylithium, 1.8 *M* in cyclohexane (0.026 mole). The mixture was warmed to room temperature and stirred for 2 hr to complete formation of the lithiohydrazide. Then, at 0°, the reaction mixture was slowly added to a solution of 7.6 g (0.062 mole) of ethyldimethylchlorosilane in 20 ml of ether, over 30 min. The reaction was stirred for 1 hr, refluxed with stirring for 2 hr, and then filtered. The filtrate on fractional distillation gave 6.2 g (81%) of colorless product, bp 98–100° (0.3 torr), $n^{22}\text{D}$ 1.5061. Gas chromatographic analysis showed the product to have an isomeric purity exceeding 99%; by nmr the product was found to be the 1,2 isomer.

Rearrangement of the 1,2 isomer with 1 equiv of *n*-butyllithium in hexane (15 hr at 25°) followed by treatment with diphenylamine gave a 10:1 mixture of 1,1 isomer:1,2 isomer, which was separated (after distillation) by preparative gas chromatography to give the pure 1,1 compound, $n^{22}\text{D}$ 1.5167. Relative retention times were 1:1.25 for the 1,2:1,1 isomers, respectively.

Anal. Calcd for $C_{14}H_{28}N_2Si_2$: C, 59.93; H, 10.06; N, 9.99; Si, 20.02. Found (1,1 isomer): C, 60.31; H, 9.55; N, 9.69. Found (1,2 isomer): C, 60.42; H, 10.14; N, 10.22.

1-Trimethylsilyl-2-methyl-2-phenylhydrazine. To a solution of 5.0 g (28 mmoles) of **7** in 25 ml of ether was added 17 ml of 1.67 *M* methyllithium in ether, at −10 to −20°. After addition was complete the reaction mixture was warmed to room temperature and then refluxed for 30 hr. Next, 5.7 g (40 mmoles) of methyl iodide in 10 ml of ether was added and the mixture was refluxed for an additional 20 hr. Work-up in the usual way gave 4.3 g (79%) of pale yellow liquid, bp 94–97° (4 torr), $n^{23}\text{D}$ 1.5145.

The product gave a single peak upon gas chromatographic analysis. The structure was assigned as that of the 1-silyl-2-methyl-2-phenyl isomer from the proton nmr, which showed a peak at τ 7.23 (Si–N–H) but none near τ 5.1 (Ph–N–H).

Anal. Calcd for $C_9H_{16}N_2Si$: C, 61.80; H, 9.33; N, 14.22; Si, 14.45. Found C, 61.81; H, 9.45; N, 14.39; Si, 14.18.

Acknowledgments. The authors thank the National Science Foundation for a grant enabling purchase of the nmr spectrometer used in these studies, the U. S. Educational Commission (Japan) for a travel grant to M. I., and Mr. H. F. Stewart for assistance in preparing and studying one of the compounds described herein.

New Anionic Rearrangements. IV. Kinetics of Catalyzed Anionic Rearrangement of Bis(organosilyl)methylhydrazines[1]

Robert West, Mitsuo Ishikawa, and Robert E. Bailey

Contribution from the Department of Chemistry, The University of Wisconsin, Madison, Wisconsin. *Received February 10, 1967*

Abstract: The kinetics of the *n*-butyllithium-catalyzed equilibration between 1,1- and 1,2-bis(organosilyl)methylhydrazines have been investigated, where the organosilyl groups are Me_3Si and $EtMe_2Si$. The approach to equilibrium follows first-order kinetics. The results are explained in terms of a deprotonation–rearrangement–protonation mechanism (eq 1) in which the deprotonation and protonation steps are rate limiting.

Earlier papers in this series[2-4] have described a new rearrangement reaction of hydrazines containing an organosilicon substituent, in which a silicon atom moves from one nitrogen to another. The previous paper discussed experiments which show that the reaction is relatively rapid, intramolecular, base catalyzed, and proceeds to equilibrium.[4] In this paper, we present some studies of the kinetics of the catalyzed rearrangement, which is of a complex and unusual kind, and a tentative description of the reaction mechanism.

Rearrangement of bis(trialkylsilyl)hydrazines was first investigated, but proved so rapid that it could not be followed kinetically, the half-time for equilibration being less than 1 min at 30°.[4] We therefore used bis(trialkylsilyl)methylhydrazines in the kinetic study. For these compounds equilibration half-times are typically of the order of a few minutes, so that the reaction kinetics could be studied by nmr spectroscopy. The kinetic runs were carried out in an nmr sample tube. By tracing repeatedly through the methylsilyl region, the disappearance of one isomer and formation of the other was followed quantitatively, as explained in the previous paper.[4]

In the kinetic studies, *n*-butyllithium was used as the catalyst. This base reacts rapidly and irreversibly to abstract protons from hydrazines. In our experiments, *n*-butyllithium could be shown to be consumed essentially within the time of mixing; proton transfer from the hydrazine to *n*-butyllithium is clearly much faster than the net hydrazine rearrangement. The bis(trialkylsilyl)methylhydrazide anion is known from earlier experiments to undergo rearrangement.[2,4] Because the rearrangement of organosilylhydrazines is catalyzed only by bases sufficiently strong to deprotonate the hydrazine,[4] we will assume that rearrangement takes place only through the anion, as in other intramolecular anionic rearrangements.[5]

Now consider a catalytic rearrangement reaction after the initial *n*-butyllithium has been used up. At that point the system contains only free hydrazine, hydrazide anion (*i.e.*, lithium hydrazide), and solvent. The sequence of events in rearrangement would be as outlined in eq 1.

A molecule of AH can be deprotonated by a B^- anion, as shown in eq 1, or by an A^- anion, but the latter reaction can be ignored since it leads to no net change in the system. Only deprotonation of AH by

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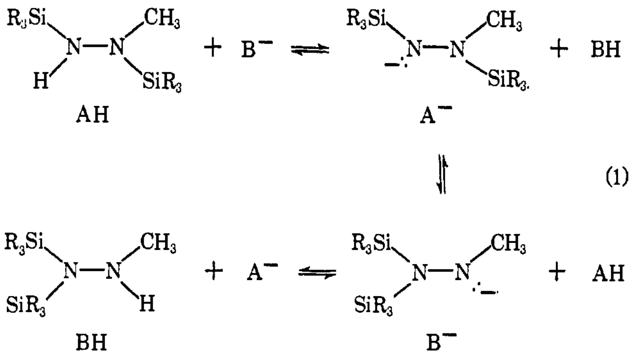
(1) Research sponsored by Air Force Office of Scientific Research (SRC), O.A.R., U.S.A.F., Grant No. AF-AFOSR 1061-66.

(2) R. E. Bailey and R. West, *J. Am. Chem. Soc.*, **86**, 5369 (1964).

(3) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **88**, 4648 (1966).

(4) R. West, M. Ishikawa, and R. E. Bailey, *ibid.*, **89**, 4068 (1967).

(5) For a summary of previously known anionic rearrangements and their mechanisms, see H. E. Zimmerman in "Molecular Rearrangement," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p 345.



B⁻ will be kinetically significant (eq 2).

$$AH + B^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BH + A^- \qquad (2)$$

Rearrangement of A⁻ to B⁻ can then take place, as indicated in eq 1, but for B⁻ to be converted to the product, BH, it must be reprotonated. Only protonation by AH is kinetically significant, and so the equation for the protonation is *identical with (2)*. An entirely similar analysis can be carried out starting with BH; then the kinetically significant steps will be the reverse of eq 2 as written. For the entire reaction, then

$$AH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} B^- \; BH \qquad (3)$$

Only the concentrations of AH and BH are known, and kinetic analysis would be impossible if it were not that *k_3 and k_4 are rapid compared to k_1 and k_2*. That rearrangement of A⁻ to B⁻ *is* extremely rapid is indicated by the nmr spectra of solutions of hydrazide anions, which show only a single Si-C-*H* peak. Even at −80°, separate resonances for A⁻ and B⁻ are not observed, although the single methylsilyl peak is somewhat broadened at this low temperature[6] (Figure 1). These observations imply that interconversion $A^- \rightleftharpoons B^-$ is rapid even compared to the proton relaxation time, and hence very rapid compared to k_1 and k_2.

Knowing that the $A^- \rightleftharpoons B^-$ step is rapid, the four unknowns, k_3, k_4, (A^-), and (B^-), can be replaced by a single equilibrium constant $K_- = (B^-)/(A^-)$. The kinetic equation reduces to eq 2, where the rate-limiting step is deprotonation of the hydrazine. The concentrations of A⁻ and B⁻ are constant with time, so the apparent rate of approach to equilibrium starting from either pure component should be first order. The expected rate equation is

$$\frac{d(BH)}{dt} = k_1(AH)(B^-) - k_2(BH)(A^-) \qquad (4)$$

If only isomer AH is present at the beginning, and if the anion concentration is negligible, then $(AH)_0 - (AH) = (BH)$, where $(AH)_0$ is the initial concentration of AH. Substituting, we obtain

$$\frac{d(BH)}{dt} = k_1[(AH)_0 - (BH)](B^-) - k_2(BH)(A^-) \qquad (5)$$

and substituting K_- for $(B^-)/(A^-)$

$$\frac{d(BH)}{dt} = (A^-)[k_1K_-(AH)_0 - (k_1K_- + k_2)(BH)] \qquad (6)$$

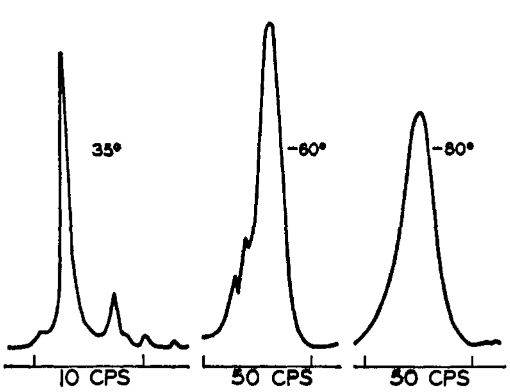


Figure 1. Silylmethyl region of nmr spectrum of anion from 1,2-bis(ethyldimethylsilyl)hydrazine in toluene solution at various temperatures.

At equilibrium

$$k_1(AH)_e(B^-) = k_2(BH)_e(A^-) = k_1[(AH)_0 - (BH)_e]K_-(A^-) \qquad (7)$$

where the subscript e refers to the equilibrium isomer concentration. $(AH)_0$ is then given by

$$(AH)_0 = \frac{(k_2 + k_1K_-)(BH)_e}{k_1K_-} \qquad (8)$$

and eq 6 can be written as

$$\frac{d(BH)}{dt} = (A^-)(k_2 + k_1K_-)[(BH)_e - (BH)] \qquad (9)$$

Integration of the above equation yields the rate equation

$$-\ln\{[(BH)_e - (BH)]/(BH)_e\} = (A^-)(k_1K_- + k_2)t \qquad (10)$$

Both (A^-) and K_- are constant, so (10) can be rewritten in the following form

$$-\ln\{[(BH)_e - (BH)]/(BH)_e\} = k_{AH}t \qquad (11)$$

where $k_{AH} = (A^-)(k_1K_- + k_2) = k_1(B^-) + k_2(A^-)$.

If BH is the starting material instead of AH, a similar derivation gives a rate expression analogous to (11)

$$-\ln\{[(AH)_e - (AH)]/(AH)_e\} = k_{BH}t \qquad (12)$$

with the rate constant $k_{BH} = (B^-)(k_2/K_- + k_1) = k_1(B^-) + k_2(A^-)$. Therefore, for equal catalyst concentration, $k_{BH} = k_{AH}$ and the *rate of the forward and reverse rearrangement should be equal.*

Experimental Section

Materials. All chemicals were reagent grade materials. Cyclohexane, benzene, and mesitylene, used as solvents, were further purified by lengthy refluxing over sodium, fractional distillation, and further refluxing over sodium. Di-*n*-butyl ether was treated in the same way but was redistilled a second time before use 1,2-Dimethoxyethane was dried over lithium aluminum hydride and fractionally distilled from it just before use.

The hydrazines were prepared as described in earlier papers[3,4] in this series, and the purified samples were stored in sealed tubes until used. *n*-Butyllithium in cyclohexane was obtained from the Foote Mineral Co.; its concentration was determined by titration.[7]

Rate Experiments. Varian proton nmr sample tubes were carefully washed with various solvents and dried. Before use, they were heated in a flame while dry nitrogen was passed through to

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[6] The line broadening at low temperatures provides evidence for the existence of two isomers of the anion, and against a single anionic intermediate with a pentacoordinate silicon equally bound to both nitrogens of the hydrazine.

[7] H. Gilman and A. H. Hauben, *J. Am. Chem. Soc.*, **66**, 1515 (1944).

Table I. Nmr Rate Data for Rearrangement of $EtMe_2SiNHN(Me)SiMe_2Et$, 0.40 *M*, with 0.108 *M* *n*-BuLi

Time, sec	Peak height, cm 1,1 isomer (BH)	 1,2 isomer (AH)	$(BH)_e - (BH)$,[a] cm	$\text{Log}\left[\frac{(BH)_e - (BH)}{(BH)_e}\right] \times 10^2$
62	2.66	18.95	7.96	1.86
110	4.12	17.36	6.50	1.79
152	5.53	16.34	5.09	1.68
194	6.74	14.63	3.88	1.57
242	7.92	13.84	2.70	1.40
282	8.60	13.13	2.02	1.28
325	9.16	12.81	1.46	1.15
384	9.62	11.85	1.00	0.97
435	9.95	11.47	0.67	0.80
481	10.25	11.28	0.37	0.54
531	10.43	11.33		
586	10.75	11.00		
638	10.69	11.01		

[a] $(BH)_e$ = 10.62 cm.

Table II. Rate Constants and Half-Times for Rearrangement of Bis(organosilyl)methylhydrazines

Hydrazine, *M*	Solvent	*n*-BuLi, *M*	$10k^3{}_{AH}$, sec^{-1}	$t_{1/2}$, sec
$EtMe_2SiNHN(Me)SiMe_2Et$				
0.40	C_6H_{12}	0.036	4.2	166
0.40	C_6H_{12}	0.072	5.3	132
0.40	C_6H_{12}	0.108	6.4	97
0.59	C_6H_{12}	0.108	9.7	70
0.80	C_6H_{12}	0.072	8.3	80
0.40	7benzene:$2C_6H_{12}$[a]	0.036	9.6	72
0.40	7mesitylene:$2C_6H_{12}$[a]	0.036	9.8	71
0.40	7*n*-Bu_2O:$2C_6H_{12}$[a]	0.036	69	10
0.40	7glyme:$2C_6H_{12}$[a]	0.036	>90	<8
0.40	C_6H_{12}:1 × 10^{-5} *M* glyme	0.036	15	46
0.40	C_6H_{12}:2 × 10^{-5} *M* glyme	0.036	26	27
0.40	C_6H_{12}:5 × 10^{-5} *M* glyme	0.036	43	16
$(EtMe_2Si)_2NNHMe$				
0.40	C_6H_{12}	0.072	4.9	141
0.40	C_6H_{12}	0.108	5.9	117
$Me_3SiNHN(Me)SiMe_3$				
0.43	C_6H_{12}	0.036	12.5	55
0.215	C_6H_{12}	0.036	4.5	153
0.108	C_6H_{12}	0.036	3.6	191
$(Me_3Si)_2NNHMe$				
0.43	C_6H_{12}	0.036	7.5	93
0.215	C_6H_{12}	0.036	4.7	163
0.108	C_6H_{12}	0.036	3.6	190

[a] Volume ratios.

remove the last traces of water from the inside. They were then capped with a rubber septum.

In a typical experiment, 1.0 ml (0.40 mmole) of 1,2-bis(ethyldimethylsilyl)methylhydrazine was mixed with 7.0 ml of cyclohexane in a 15-ml flask, dried as described above for the sample tubes. Then 0.80 ml of the solution was transferred to the sample tube, and the nmr spectrum of the sample was taken to ensure optimum instrumental settings of the Varian A-60 spectrometer.

A 0.20-ml of portion of the commercial *n*-butyllithium solution, diluted to 0.18 *M* with cyclohexane, was then injected into the nmr tube with a long needle. The timer was started as the catalyst was injected. The tube was shaken for 20 to 30 sec and then placed in the nmr probe; the silylmethyl region (about 10 cycles) was scanned repeatedly, using 100-cycle sweep width and 250-sec sweep time settings. All runs were at 35°.

The peak heights above the base line were then measured to find the concentrations of 1,1 and 1,2 isomers at the time of each scan. More elaborate methods to obtain the area of the peak gave no difference in the results. The measurement precision is estimated as ±2%.

Typical data for a kinetic run are given in Table I.

Results and Discussion

In order to obtain reaction rates, plots were made of $\log (C_e - C)/C_e$ *vs.* time, where C_e and C are the equilibrium and actual isomer concentration, according to eq 11 and 12. Typical plots are shown in Figures 2–4. Excellent straight lines were obtained in all cases, showing that the approach to equilibrium is kinetically a first-order process. Figure 2 shows data from three different runs under the same conditions of concentration, showing the reproducibility. Data from all kinetic runs are summarized in Table II, which gives results both in terms of half-times for equilibration and rate constant k_{AH} or k_{BH} of eq 11 and 12.

A comparison of the forward and reverse rate constants for rearrangement, k_{AH} and k_{BH}, provides a test of the kinetic model. From the data in Table II, it is apparent that at 0.40 *M* hydrazine, k_{AH} and k_{BH} for the bis(ethydimethylsilyl)methylhydrazines conform to the model fairly well, in that they differ by less than 10%. At a similar concentration, however, k_{AH} and k_{BH} for the bis(trimethylsilyl)methylhydrazines differ by a factor of 1.7 (Figure 4). But if the initial concentration of hydrazine isomer is reduced, the forward and reverse rate constants become more nearly equal, and at 0.108 *M* hydrazine concentration they are indistin-

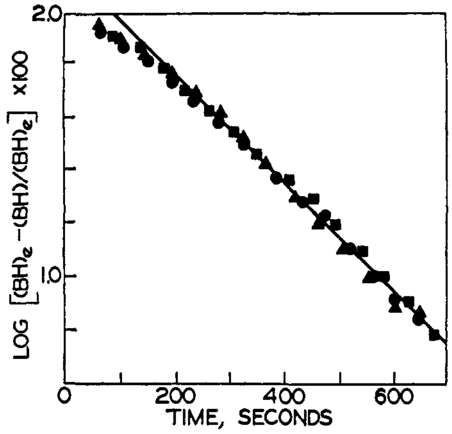


Figure 2. Equilibration of 1,2-bis(ethyldimethylsilyl)methylhydrazine, 0.40 *M*, with 0.036 *M* *n*-BuLi in cyclohexane. Plot shows data from three runs on the same set of axes, showing reproducibility.

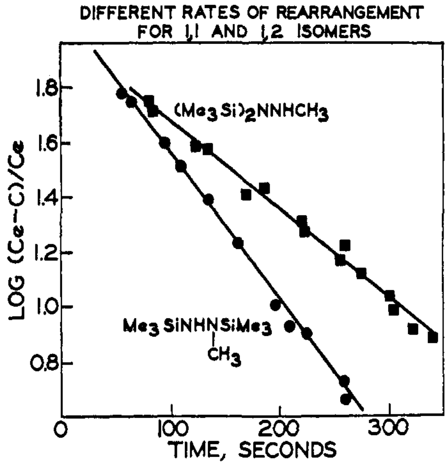


Figure 4. Kinetics of rearrangement of bis(trimethylsilyl)methylhydrazines, showing different rate for forward and reverse reaction: 0.43 *M* hydrazine, 0.036 *M* *n*-BuLi in cyclohexane.

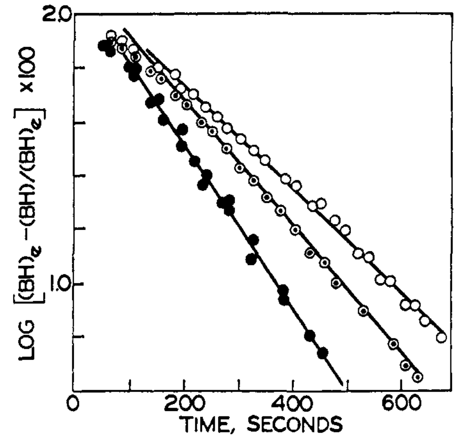


Figure 3. Equilibration of 1,2-bis(ethyldimethylsilyl)methylhydrazine, 0.40 *M* in cyclohexane, showing effect of base concentration on rate: ○, 0.036 *M* *n*-BuLi; ⊙, 0.072 *M* *n*-BuLi; ●, 0.108 *M* *n*-BuLi.

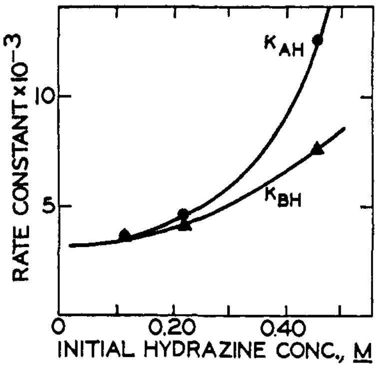


Figure 5. Rate constants K_{AH} and K_{BH} for forward and reverse rearrangement of 1,2-bis(trimethylsilyl)hydrazine, as a function of hydrazine concentration.

guishable within experimental error (Table II, Figure 5).

The results are thus generally consistent with the kinetic model for low hydrazine concentration but deviate as the hydrazine concentration increases, at least for the trimethylsilyl compounds. It is also evident that the rate constant increases sharply with increasing hydrazine concentration, a fact which seems inconsistent with eq 9 and with the first-order kinetics of the equilibration.

Our interpretation is that excess hydrazine serves as a specific solvating agent for the lithium cation in the ion pair, promoting more rapid protonation. The 1,2 isomer of bis(trimethylsilyl)methylhydrazine evidently is a better solvating base than the 1,1 isomer, so the kinetic acceleration is greater for rearrangement of the 1,2 compound. The difference between k_{AH} and k_{BH} is less pronounced for the ethyldimethylsilyl compounds, probably because the ethyl groups introduce steric restrictions which limit solvation of the lithium ion.

A specific solvation effect is also indicated by the rate data in different solvents (Table II). 1,2-Bis(ethyldimethylsilyl)methylhydrazine was used as the substrate for studies of the effect of base concentration and solvent on the rate. The equilibration rate for this compound is increased by a factor of 2.3 when the cyclohexane solvent is largely replaced by benzene or mesitylene. Basic solvents give much more pronounced rate enhancement; a 16-fold increase is observed with di-*n*-butyl ether and more than 20-fold with 1,2-dimethoxyethane (glyme), which is known to be a good solvating agent for Li^+. Moreover, extremely small amounts of glyme increase the rate markedly. The fact that as little as 1×10^{-5} *M* glyme, with 0.4 *M* hydrazine and 0.036 *M* *n*-BuLi, increases the rate by a factor of 3.6 strongly suggests a specific solvation effect. Probably excess hydrazine and basic solvents like glyme act in the same way to solvate the lithium cation in the lithium hydrazide ion pair, and so promote proton exchange according to eq 2.

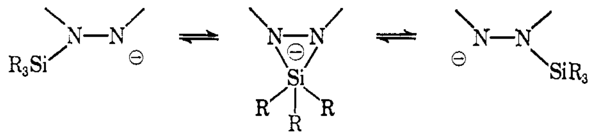
Increasing the *n*-butyllithium concentration increases the rate of rearrangement, the kinetic dependence for 1,2-bis(ethyldimethylsilyl)methylhydrazine being about 0.3 in base. From eq 11, k_{BH} should be linearly dependent on the total base concentration. The observed low dependence on $(A^-) + (B^-)$ suggests still further complexities in the reaction. Perhaps larger ion aggregates are formed at high base concentration, which are less effective deprotonating agents.

In the preceding paper it was shown that at equilibrium $(AH)_e \cong (BH)_e$ for the compounds under discussion. Because at equilibrium $k_1(AH)_e(B^-) = k_2$-

$(BH)_e(A^-)$, it follows that $k_1(B^-) \cong k_2(A^-)$. Independent information about the ratio $(A^-)/(B^-)$, not presently available, would be necessary in order to obtain actual values of k_1 and k_2.

Reaction Mechanism. Results of the kinetic experiments are generally consistent with the model proposed in eq 1, in which equilibration of hydrazine isomers is effected by deprotonation, anion rearrangement, and reprotonation. Other 1,2 anionic rearrangements are known,[6] but none have been found to proceed catalytically as the hydrazine rearrangement does. Most anionic rearrangements involve movement of a substituent from one kind of atom to another kind, the best known being the Stevens (N → C) and Wittig (O → C) rearrangements. Such rearrangements generally proceed irreversibly to produce a much more stable anion and are usually quite slow. The other reaction most closely related to ours is the C → C rearrangement of substituted ethanes, discovered independently by Grovenstein[8] and Zimmerman.[9,10] The kinetics of this reaction have not been studied, but it is clearly much slower than rearrangement of the silylhydrazide anions. In fact, we estimate that the silylhydrazine rearrangement proceeds, at the minimum, 10^6 faster than any previously known anionic rearrangement.

In intramolecular 1,2 anionic rearrangements, the transition state is thought to involve bridging by the migrating group, which must at some point be equally bonded to the 1 and 2 atoms. The energy of activation for migration of an organosilicon substituent could be much less than for other bridging groups, because of the availability of 3d orbitals on silicon which permit easy expansion of covalence from four to five.[11]



These considerations suggest that silyl groups should be exceptionally mobile in other anionic rearrangements, a possibility which is now being tested.

Acknowledgment. M. I. thanks the United States Educational Commission (Japan) for a travel grant.

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(8) E. Grovenstein, Jr., *J. Am. Chem. Soc.*, **79**, 4985 (1957).

(9) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957).

(10) H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

(11) There is much indirect evidence for pentacoordinate intermediates in organosilicon chemistry, and at least one stable pentacoordinate triorganosilicon species has been isolated;[12] see L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

(12) J. Y. Corey and R. West, *J. Am. Chem. Soc.*, **85**, 4034 (1963).

Skeletal Rearrangements of the Methyl-7,7-dicyanonorcaradienes[1]

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Abstract: Skeletal rearrangements of methyl-substituted 7,7-dicyanonorcaradienes occur at temperatures above 55° and are shown to be intramolecular. Isotopic position-labeling experiments are consistent with a circumambulatory mechanism. The major competing process is aromatization, which seems to be fast enough to prevent observation of any significant amount of cyano group shift. The drastic reduction (*ca.* 18 kcal/mole) in activation energy for the circumambulatory process produced by changing 7,7-dimethyl to 7,7-dicyano substitution is attributable to elimination of the endothermic preliminary tropilidene → norcaradiene step and to weakening of the C-1–C-7 bond in the cyano cases.

At temperatures near 300°, skeletal rearrangements interconvert *x*,7,7-trialkyltropilidenes (cycloheptatrienes) by way of a mechanism that probably involves preliminary valency tautomerism to the corresponding norcaradienes (bicyclo[4.1.0]heptadienes).[3,4] The endothermic preparatory step adds an estimated 7–15 kcal/mole to the activation energy for the skeletal rearrangement. True norcaradienes presumably would not be required to pay this energy increment and therefore should rearrange at much lower temperatures. The recent discovery by Ciganek[5] that the products of reactions of dicyanodiazomethane with aromatic hydrocarbons are 7,7-dicyanonorcaradienes rather than 7,7-dicyanotropilidenes makes possible a test of this question.

The Toluene–Dicyanodiazomethane Reaction. Thermolysis of a solution of dicyanodiazomethane[6–8] in

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(2) (a) National Institutes of Health Postdoctoral Fellow, 1966–1967; (b) National Institutes of Health Postdoctoral Fellow, 1964–1965.

(3) (a) J. A. Berson and M. R. Willcott, III, *J. Am. Chem. Soc.*, **87**, 2751 (1965); (b) *ibid.*, **87**, 2752 (1965); (c) *ibid.*, **88**, 2494 (1966).

(4) J. A. Berson and M. R. Willcott, III, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **27**, 139 (1966).

(5) E. Ciganek, *J. Am. Chem. Soc.*, **87**, 652, 1149 (1965).

(6) We are greatly indebted to Dr. Ciganek for information on the preparation[7] and reactions[8a] of this material in advance of publication as well as for helpful discussions of the chemistry of the dicyanonorcaradienes.[8b]

(7) E. Ciganek, *J. Org. Chem.*, **30**, 4198 (1965).

(8) (a) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1454 (1967); (b) *ibid.*, **89**, 1458 (1967).